Light Emission Mechanism of $Lu_2(SiO_4)O$:Ce

H. Suzuki* and T. A. Tombrello
Division of Physics, Mathematics, and Astronomy,
California Institute of Technology, Pasadena, California, 91125

C. L. Melcher and J. S. Schweitzer
Schlumberger-Doll Research, Old Quarry Rd., Ridgefield, CT 06877-4108

Abstract

Lutetium oxyorthosilicate $Lu_2(SiO_4)O$ has two crystallographically independent lutetium sites. When it is doped with Ce, the dopant Ce is assumed to occupy two different sites and thus the existence of two activation centers (called "Ce1" and "Ce2") was proposed. UV and gamma-ray excited spectra clearly indicate that two activation centers exist in cerium-doped lutetium oxyorthosilicate $Lu_2(SiO_4)O$:Ce (LSO).

I. INTRODUCTION

Ce-doped lutetium oxyorthosilicate (LSO) was recently introduced as a potential single crystal scintillator [1], which has a high density, high effective atomic number for efficient gamma-ray detection, reasonably high light output and fast scintillation decay time, compared with conventional scintillators such as NaI(Tl) and bismuth germanate $Bi_4Ge_3O_{12}$. When LSO is excited by gamma-ray radiation, it has a decay constant of ~40 ns. Although many inorganic scintillators have longer decay components as well as the shorter component, no longer decay components, at a level of 0.1% of the initial intensity, have been observed for LSO within 3 μs of excitation [1].

The host material $Lu_2(SiO_4)O$ is one of the oxyorthosilicates $RE_2(SiO_4)O$ (RE = rare earth) [2] which display two different structure types. One structure type is stable for the large rare earths, La to Tb, and forms the monoclinic structure of space group $P2_1/c$. The rare earths in this structure occupy two crystallographically different sites. One site has an oxygen coordination number of 7 and the other site has 9. The other structure type includes the smaller rare earths, Dy to Lu, and has the monoclinic structure of space group C2/c [3]. The rare earths in this group have 6 or 7 oxygen ligands. $Lu_2(SiO_4)O$ belongs to the latter group, namely, the monoclinic structure C2/c.

When $RE_2(SiO_4)O$ is doped with Ce, the Ce substitutes for the host rare earth and exists as Ce^{+3} ion. The Ce^{+3} ion has one electron in the 4f shell, and the light emission is based on the electronic transition from the lowest 5d energy level to two 4f ground levels, which have an energy separation of ~2253 cm^{-1} from the spin-orbit interaction [4]. The typical decay time of Ce^{+3} is of the order of tens of nanoseconds [5]. Since there are two crystallographically independent rare earth sites in $RE_2(SiO_4)O$, it is reasonable to assume that there are also two Ce^{+3} sites in $RE_2(SiO_4)O$:Ce. In fact, our previous study [6] revealed that Ce-doped gadolinium oxyorthosilicate $Gd_2(SiO_4)O$:Ce (GSO), which has the $P2_1/c$ structure type, has two Ce sites and that these two activation centers contribute to the emission excited by gamma-ray radiation. Although LSO has a different structure (C2/c) than GSO ($P2_1/c$), it also has two crystallographically independent lutetium sites. Thus it is natural to assume that there are also two Ce^{+3} sites, i.e., two activation centers in LSO. The two-activation-center model has been investigated for its applicability in describing the scintillation mechanism in LSO.

The scintillation of LSO can be separated into primary processes and secondary processes [7]. The primary processes are the transfer of energy from the ionizing radiation to the luminescent centers (Ce^{+3}). The secondary processes are the processes by which excited luminescent centers lose their energy. These secondary processes can be studied independently by direct excitation of the luminescent centers using ultraviolet excitation instead of ionizing radiation. It is the secondary processes which we attempt to analyze in this paper to resolve the light emission mechanism of Ce^{+3} in LSO. The primary (energy transfer) processes will be the subject of a separate study.

II. Experiment

The LSO single crystal used in this study was grown by the Czochralski technique in our laboratory using raw materials with purities of at least 99.99%. Iridium wire was used as a seed. The Ce concentration in the melt from which the crystal was grown was 0.125% relative to the lutetium content. However, because of the large difference in the ionic radius between the Lu^{+3} ion (0.848 Å) and the Ce^{+3} ion (1.034 Å), the distribution coefficient of Ce in the crystal is very small. The Ce concentration in the crystal was analyzed by X-ray Assay Laboratories to be 0.0258% relative to Lu.
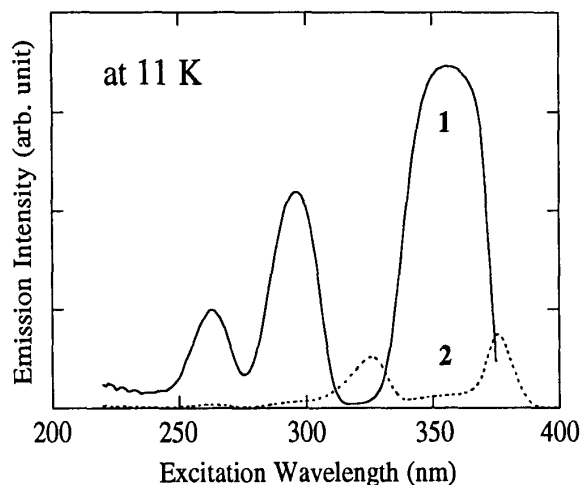
Figure 1. Excitation spectra of LSO at 11 K. The excitation spectra were measured at the two emission wavelengths of 390 nm (solid curve) and 500 nm (dashed curve).

The calculated distribution coefficient of Ce in LSO is thus ~0.2, in contrast with the greater distribution coefficient ~0.56 of Ce in GSO [8]. The structure of this crystal was analyzed by the powder x-ray diffraction method. The result confirmed that LSO had a monoclinic C structure.

The experimental equipment has been described in detail elsewhere [6]. Excitation and emission spectra between 11 and 300 K were measured with a SPEX Fluorolog-2 spectrofluorometer equipped with a helium refrigerator. For temperatures above 300 K, an LS-100 (Photon Technology International, Inc.) spectrophotometer equipped with a resistively heated copper sample holder was used. Decay time data were obtained by operating the LS-100 in a pulsed mode. Low temperature decay data were obtained by sample immersion in organic solvents frozen by liquid nitrogen. Decay data above room temperature were obtained with the same heated copper sample holder.

III. RESULTS

GSO has two crystallographically independent Gd^{+3} sites and the existence of two activation centers (Ce1 and Ce2) was proposed for the following reasons [6]:

(1) When GSO was excited with UV light, two different decay times, two types of excitation spectra and two types of emission spectra were observed.

(2) The absorption spectra have two types of Ce^{+3} absorption bands whose wavelengths correspond to the excitation bands of two different Ce^{+3} sites.

(3) The temperature-dependence of the decay times is identical with the temperature-dependence of the emission efficiencies between 11 and 300 K for each Ce^{+3} luminescence center.

(4) There exist, in fact, two crystallographically independent sites of the Ce^{+3} ion in GSO.

The confirmation of the two-activation-center model for GSO was that the gamma-ray excited emission spectra could be duplicated by adding the appropriately weighted UV-excited emissions of Ce1 and Ce2 at all temperatures between 11 and 300 K.

By analogy with GSO, UV excited emission and excitation spectra were examined for LSO. Similar to GSO, two types of excitation and emission spectra were obtained with UV-excitation. Fig. 1 shows two excitation spectra at 11 K which have emission wavelengths of 390 nm (marked "1") and 500 nm (marked "2"). The excitation spectrum "1" has excitation bands at 263, 296 and 356 nm, while spectrum "2" has excitation bands at 326 and 376 nm.

The measurements of emission spectra were made using excitation wavelengths corresponding to the strongest and lowest excitation bands in spectra "1" and "2" of Fig. 1, i.e., 356 and 376 nm. Fig. 2 displays two emission spectra excited at 356 nm (marked "1") and 376 nm (marked "2"). The spectrum"1" has two emission peaks at 393 and 427 nm, showing the characteristic transition of the Ce^{+3} ion from the 5d level to the two 4f ground states. The spectrum "2" has an emission peak at 460 nm, for which the Ce^{+3} doublet structure cannot be seen.
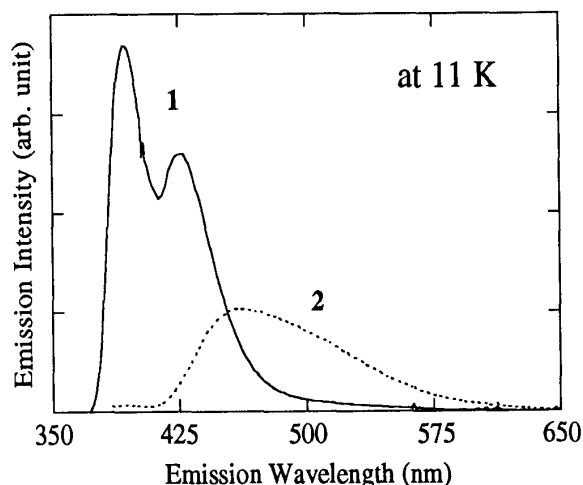

Figure 2. Emission spectra of LSO at 11 K. The two emission spectra have excitation wavelengths of 356 nm (solid line) and 376 nm (dashed line).
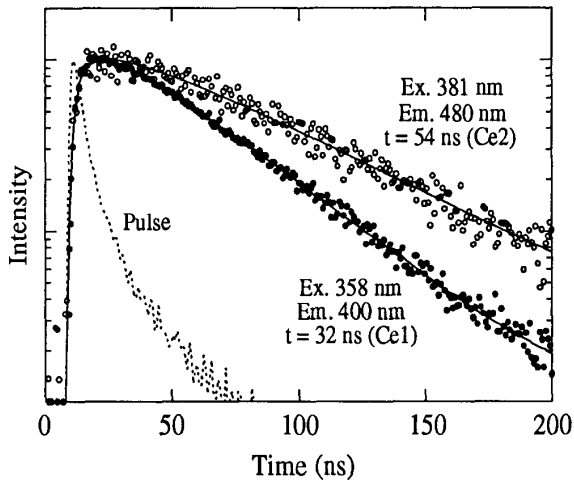
Figure 3. UV-excited decay curves of Ce1 (filled circle) and Ce2 (open circle) in LSO at 77 K. The dashed line indicates the nitrogen flash pulse. The excitation and emission wavelengths for Ce1 are 358 and 400 nm, respectively. The excitation and emission wavelengths for Ce2 are 381 and 480 nm, respectively. The solid curve are fits to the data with a single exponential (32 ns for Ce1 and 54 ns for Ce2).

Since there are two crystallographically independent sites of the Ce^{+3} ions, it is reasonable to attribute the two types of excitation and emission spectra to the two Ce^{+3} sites in LSO. For convenience, we will refer to these centers as Ce1 and Ce2. We arbitrarily designate Ce1 as the center responsible for excitation bands at 263, 296 and 356 nm (curve "1" in Fig. 1) and Ce2 as the center responsible for excitation bands at 326 and 376 nm (curve "2" in Fig. 1). It follows that the emissions at 393 and 427 nm are due to Ce1 (curve "1" in Fig. 2), and the emission at 460 nm is due to Ce2 (curve "2" in Fig. 2).

If the lowest excited level of the Ce^{+3} ions, i.e., the lowest 5d level for each site is excited by UV light, both the decay time $\tau(T)$ and luminescence efficiency $\eta(T)$, which are functions of temperature, should satisfy the characteristic fluorescence relation [9]

$$\tau(T) / \tau(0) = \eta(T) / \eta(0).$$

By comparing the temperature-dependence of the decay time and luminescence efficiency from these lowest 5d levels to the 4f ground state level, it is theoretically possible to test the existence of two luminescence centers. However, it was difficult to measure the luminescence efficiency of Ce2 above 80 K since the broadening of the Ce1 excitation band over the Ce2 excitation band becomes significant and the Ce2 emission was no longer resolved from the Ce1 emission above 80 K. In the discussion below, for the Ce2 center we present only the decay time at 77 K. And for Ce1 center both the decay time

and luminescence efficiency are displayed as a function of temperature.

Fig. 3 shows the decay time of Ce1 and Ce2 at 77 K, together with the pulse from the N_2 flash lamp, which has about a 6 ns duration and a long decaying tail. These decay curves were obtained by excitation into the lowest 5d level. The pulse shape was deconvoluted from the decay data that were then fit with a single exponential. The excitation and emission wavelengths were carefully chosen to minimize overlap of the emission curves of the two Ce sites. The decay curve of Ce1 has excitation and emission wavelengths of 358 and 400 nm, respectively. The decay curve of Ce2 has excitation and emission wavelengths of 381 and 480 nm, respectively. The solid curves are fits to the data with a single exponential. The calculated decay times are 32 ns for the Ce1 and 54 ns for the Ce2.

Fig. 4 shows the decay time (Ex.358, Em.400 nm) and luminescence efficiency (Ex.356 nm) of Ce1 as functions of temperature with the excitation into the lowest 5d level of Ce1. The rollover point of the decay time is near 300 K. This trend in the temperature-dependence of the decay time is similar to the behavior of the luminescence efficiency.

IV. DISCUSSION

The temperature-dependence of decay time and luminescence efficiency in GSO were shown for each center [6]. In GSO the temperature-dependence of Ce1 was different than that of Ce2 so that it was clear that there were two activation centers in GSO. In LSO, however, the spectra of Ce2 cannot be well resolved above 80 K and the existence of Ce2 cannot be confirmed.
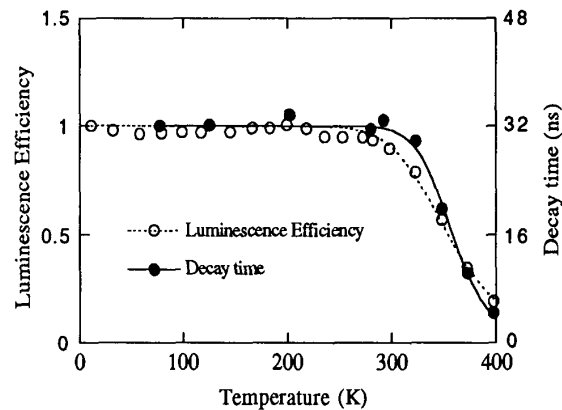

Figure 4. The decay time (filled circle) and the luminescence efficiency (open circle) of Ce1 in LSO as functions of temperature. The emission intensity and decay time obtained at each temperature was normalized to the intensity at 11 and 77 K, respectively.
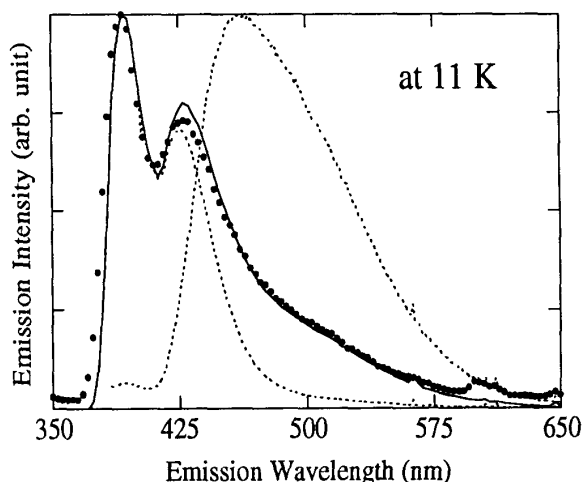
Figure 5. The gamma-ray excited emission (filled circle), the UV-excited emissions of Ce1 (excited at 356 nm) and Ce2 (at 376 nm) (dashed lines), and a weighted combination of the Ce1 and Ce2 emissions (solid line) for LSO at 11 K. All the measured spectra are normalized to their peak intensity.

However, the fact that the gamma-ray excited emission curve can be simulated by the UV excited emissions of Ce1 and Ce2 supports the existence of two activation centers. Fig. 5 shows the gamma-ray (^{241}Am) excited emission, UV-excited emissions of Ce1 and Ce2, and a weighted combination of the Ce1 and Ce2 emissions for LSO at 11K. This calculated emission spectrum was obtained by adding the emission spectra of Ce1 and Ce2 in a ratio of 55:45.

It is clear from Fig. 5 that the solid curve simulated with Ce1 and Ce2 emissions fits the gamma-ray excited emission curve. This agreement supports our assumption that there are two activation centers in LSO.

V. SUMMARY

Two types of excitation and emission spectra with UV-excitation were shown at 11 K for LSO. Since there are two crystallographically independent lutetium sites in LSO, the existence of two Ce activation centers (two-activation-center model) was proposed. The existence of two different decay time constants of the order of tens of nanosecond, which are characteristic for fast Ce emission, were shown at 77 K. Although the temperature-dependence of the decay time and the luminescence efficiency could not be measured for the Ce2, the fact that the gamma-ray excited emission can be reconstructed from a weighted combination of the Ce1 and Ce2 emission spectra supports the two-activation-center model for LSO.

VI. REFERENCES

* Present address: Schlumberger-Doll Research, Old Quarry Road, Ridgefield, CT 06877-4108.

[1] C. L. Melcher and J. S. Schweitzer, A promising new scintillator: cerium-doped lutetium oxyorthosilicate, Nucl. Instr. and Meth. A314, 212-214 (1992). C. L. Melcher, Lutetium orthosilicate single crystal scintillator detector, U. S. Patent No. 4,958,080, (1990) and 5,025,151 (1991).

[2] J. Felsche, The crystal chemistry of the rare-earth silicates, in Structure and Bonding V13, Springer-Verlag, 99-197 (1973).

[3] C. D. Brandle, A. J. Valentino and G. W. Berkstresser, Czochralski growth of rare-earth orthosilicates (Ln$_2$SiO$_5$), J. Cryst. Growth, 79, 308-315 (1986).

[4] B. G. Wybourne, Spectroscopic properties of rare earths, Page 41, John Wiley & Sons, Inc. (1965).

[5] L. Lyu and D. S. Hamilton, Radiative and nonradiative relaxation measurements in Ce^{3+} doped crystals, J. Lumin. 48 & 49, 251-254 (1991).

[6] H. Suzuki, T. A. Tombrello, C. L. Melcher and J. S. Schweitzer, UV and gamma-ray excited luminescence of cerium-doped rare earth oxyorthosilicates, Nucl. Instr. and Meth. A320, 263-272 (1992).

[7] J. B. Birks, The theory and practice of scintillation counting (Pergamon, 1964).

[8] C. L. Melcher, R. A. Manente, C. A. Peterson and J. S. Schweitzer, Czochralski growth of rare earth oxyorthosilicate single crystal, J. Cryst. Growth, in press.

[9] D. Curie, Luminescence in crystals, Page 4, John Wiley & Sons Inc. (1963).